BYU

ADDRESSING HETEROGENEITY IN ELECTRODE FABRICATION PROCESSES

Dean R. Wheeler and Brian A. Mazzeo
Brigham Young University

June 12, 2019

Project ID # bat220

OVERVIEW

Timeline

- Project start date: Oct 2016
- Project end date: Sep 2019
- Percent complete: 83%

Budget

- Total project funding: $1,050,000
  (DOE share 100%)
- Funding received in FY18: $350,000
- Funding for FY19: $350,000 (12 months)

Barriers

XFC capable EV cells

- $75/kWh cost
- 300 W/kg (10 s) power
- 350 Wh/kg (C/3) energy

Partners

- Industrial collaborations with Navitas, K2, Eagle Picher, Hydro-Québec, and others
- Research collaborations with ANL, NREL, LBNL, UC Irvine, and others

RELEVANCE

- **Program Objectives:**
  - Better understand connections between fabrication conditions and undesired heterogeneity of thin-film electrodes by means of new non-destructive inspection techniques and computer models
- **Current-Year Objectives:**
  - Map localized electronic and ionic heterogeneity on commercial electrodes
  - Incorporate heterogeneity into models of overall cell performance
  - Refine microstructure simulation models to investigate physics of drying
- **Impact on DOE Barriers for EVs/XFC EVs:**
  - This work addresses a longstanding unmet industry need to be able to conveniently measure physical properties of thin-film electrodes and detect manufacturing variations and changes during cycling—solving this problem will accelerate process improvement, reduce scrap rates, and lower battery costs
  - Extreme Fast Charging requires adequate transport of ions and electrons throughout the electrode—this work provides experimental and modeling tools to analyze the effect of processing on transport pathways
- **Broader Impacts of This Work:**
  - This work will improve Li-ion battery technology in EVs and at the grid-scale, which will reduce energy costs to businesses and consumers, increase energy security, and allow clean energy technology to move people and goods

MILESTONES

2018

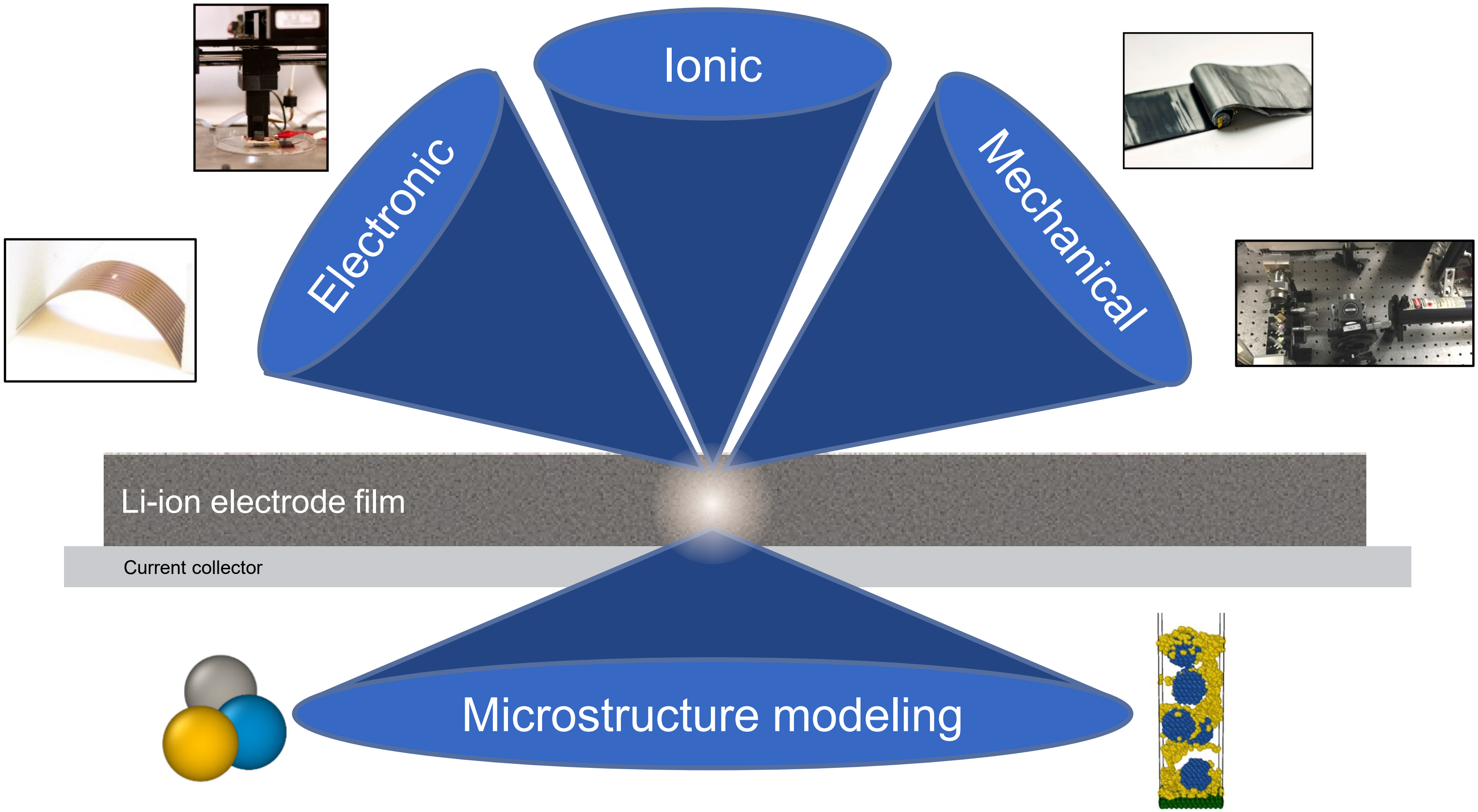
- **3Q**: (Go/No-Go) Demonstrate that localized ionic conductivity probe has adequate reliability for continued development. *Complete / Go*
- **4Q**: Quantify the durability of flex probes to validate suitability for industrial use. *Complete*

2019

- **1Q**: Quantify microstructure heterogeneity effects on overall cell performance. *Complete*
- **2Q**: Create localized ionic conductivity maps for two candidate materials. *Complete*
- **3Q**: Create design package for commercialization of the conductivity probe including associated control and computing hardware. *Complete*
- **4Q**: Demonstrate the capacity of the smoothed particle hydrodynamics drying model to investigate the physics of the drying process for further optimization. *On track*

Any proposed future work is subject to change based on funding levels.

APPROACH



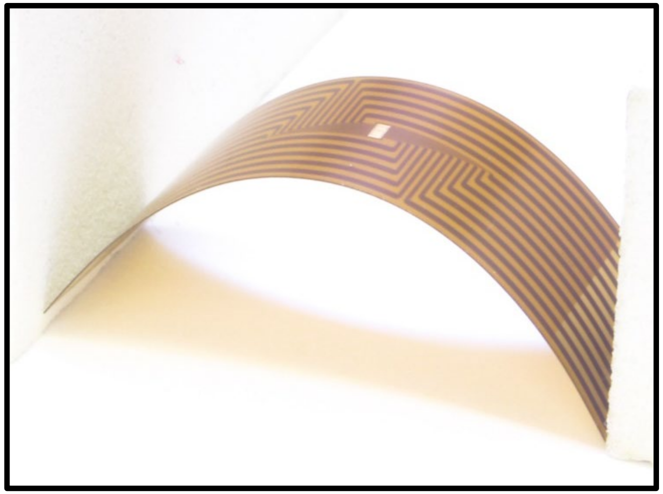
Building tools and models to address heterogeneity in Li-ion electrodes.

APPROACH

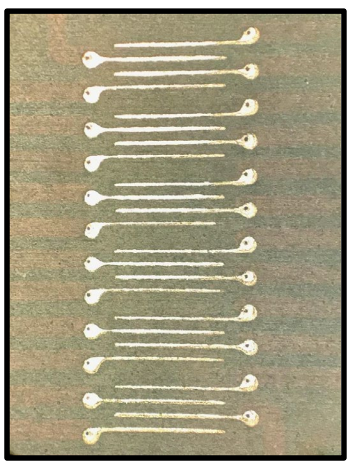
We propose to enable improved electrode manufacturing processes by rapid feedback on transport and mechanical problems associated with the microstructural arrangement of particles. A range of new experimental and modeling tools have been developed to measure and predict *localized* properties.

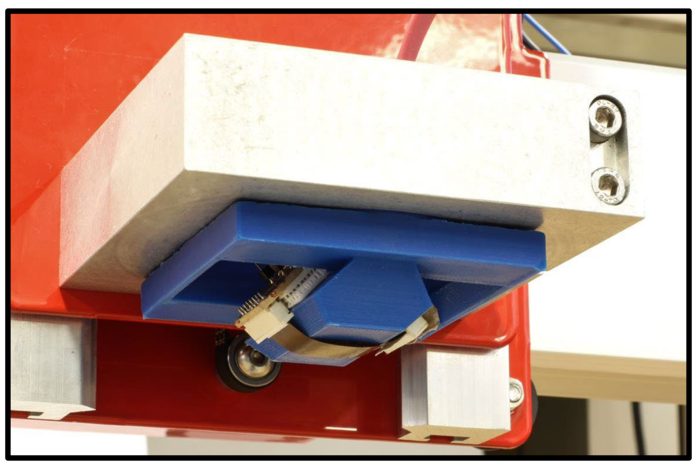
- Construct novel micro-N-line surface probes that can sample local conductivity of intact battery electrodes
- Experimentally compare tradeoffs of and effects on electronic and ionic transport (collaborations with NREL, ANL, Navitas, K2, others)
- Construct a first-principles particle-dynamics model that can predict electrode microstructure and conductive pathways
- Construct a laser-based acoustic probe for rapidly determining mechanical properties of electrode films

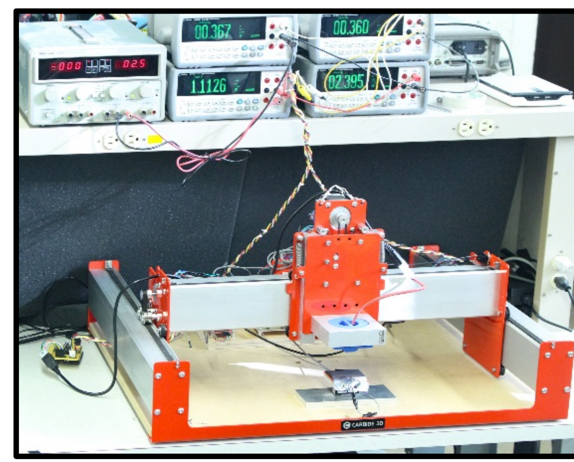
Previous Technical Accomplishment (FY18): Second-Generation Flexible Probe



A second-generation flexible micro-line probe was developed using a commercial flexible printed circuit board process. The probe was then incorporated into a low-cost, large-format stage to perform localized conductivity measurements on battery electrode films, yielding similar quality of results as more-expensive prior designs.

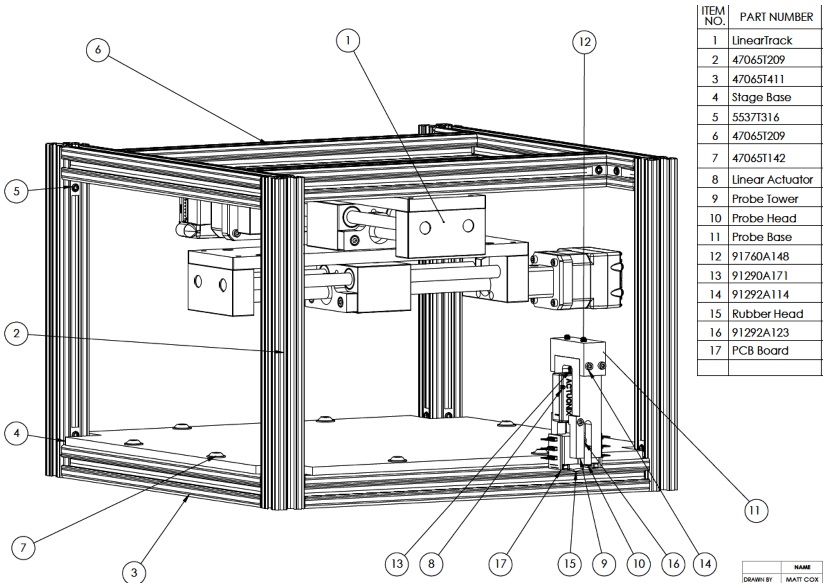




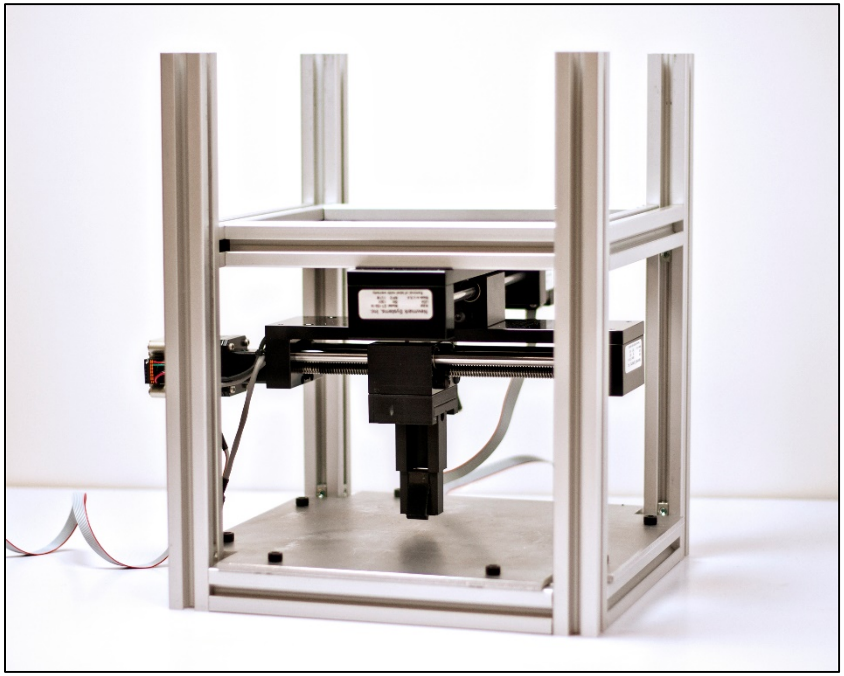


A micro-sized set of lines contacts the sample and permits electrical measurement; location is changed by computer-controlled actuators

Technical Accomplishment: Design Package for Commercialization of Conductivity Probe



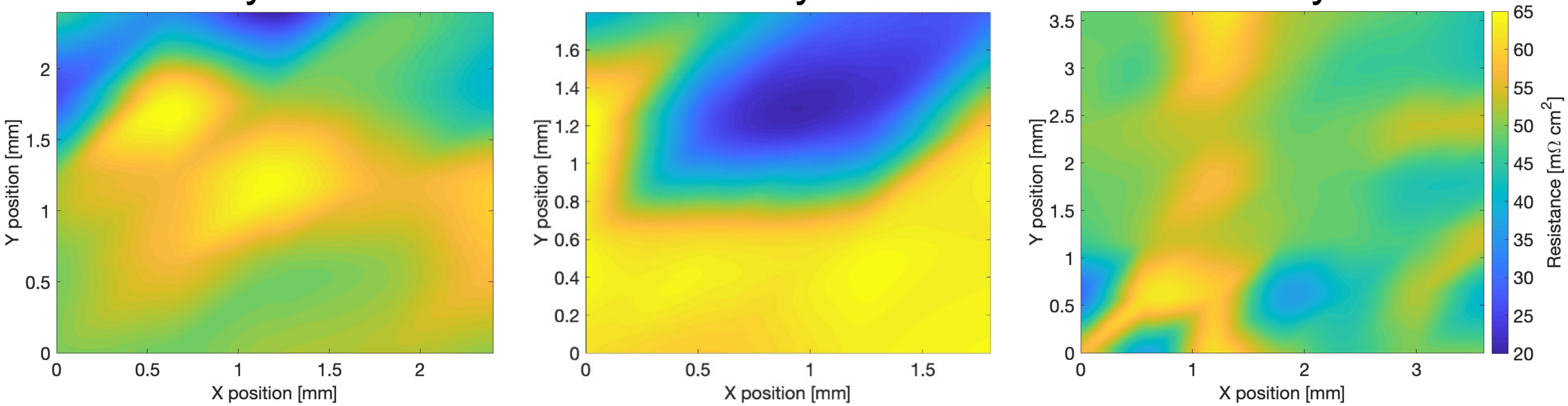
ITEM NO.	PART NUMBER
1	LinearTrack
2	47065T209
3	47065T411
4	Stage Base
5	5537T316
6	47065T209
7	47065T142
8	Linear Actuator
9	Probe Tower
10	Probe Head
11	Probe Base
12	91760A148
13	91290A171
14	91292A114
15	Rubber Head
16	91292A123
17	PCB Board



A student team designed and built a self-contained testing unit with a combination of off-the-shelf and customized parts, and built associated operating software. Probes and software (not the complete system) were sold to Missouri S&T and UC Irvine this year. Discussions with multiple companies are ongoing to further commercialize the conductivity probe.

Technical Accomplishment: Electronic Measurement of Electrodes after Cycling

3 cycles | 600 cycles | 1650 cycles

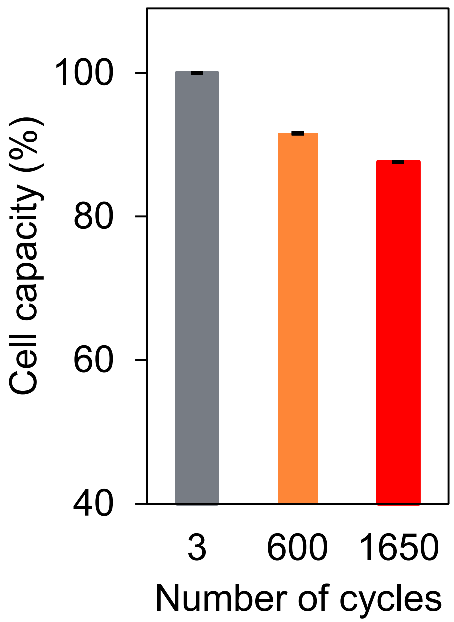


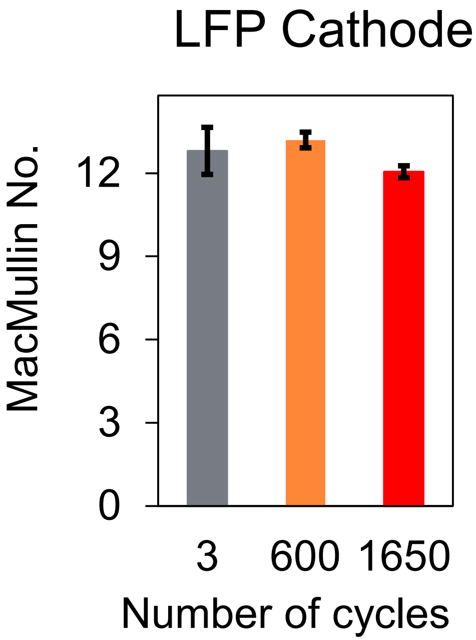
49.6 ± 4.6 mΩ·cm^2 | 51.1 ± 8.7 mΩ·cm^2 | 49.5 ± 1.9 mΩ·cm^2

(Average ± 95% CI)

Electronic measurements were made on LFP electrode films harvested from K2-made 18650 batteries that had been deep-cycled. No significant degradation of electronic conductivity was observed in contrast to LCO cathodes tested in FY18.

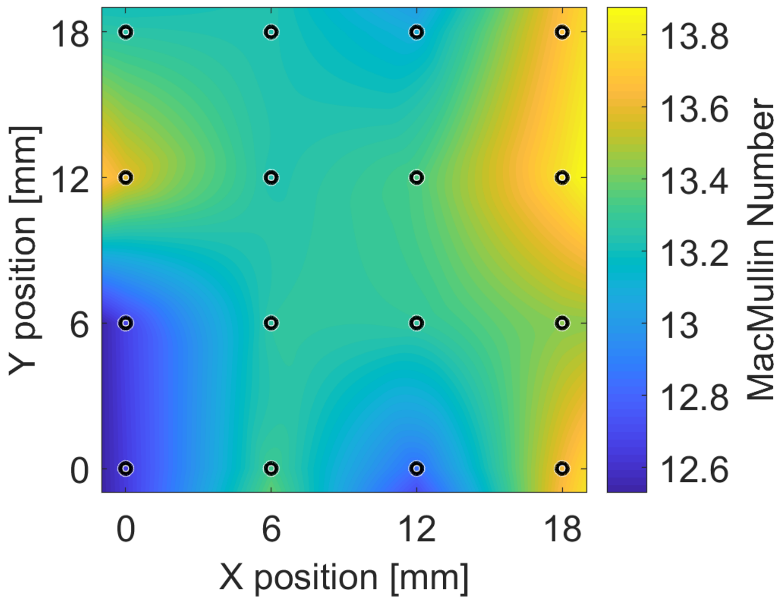
Technical Accomplishment: Ionic Measurement of Electrodes after Cycling



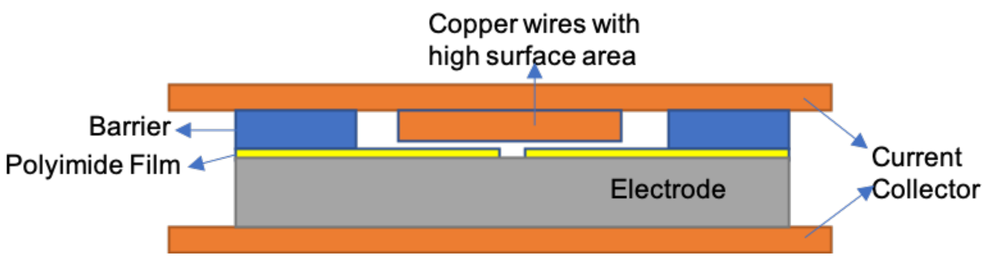


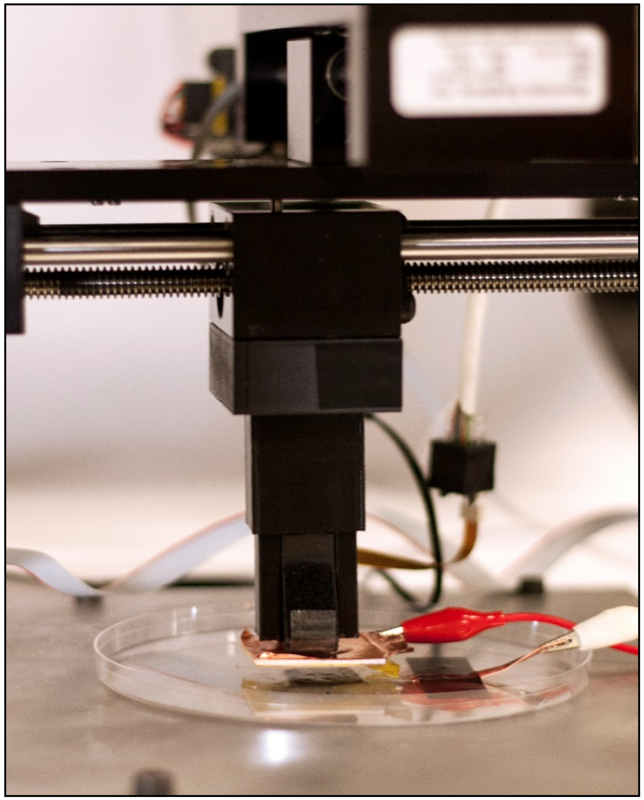
The K2-made cells (see previous slide) maintained 88% capacity after 1650 deep cycles. No significant degradation of average ionic conductivity (MacMullin number) in harvested LFP electrodes was observed, which is similar to LCO electrodes tested in FY18.

TECHNICAL ACCOMPLISHMENT: LOCALIZED IONIC CONDUCTIVITY MAPPING



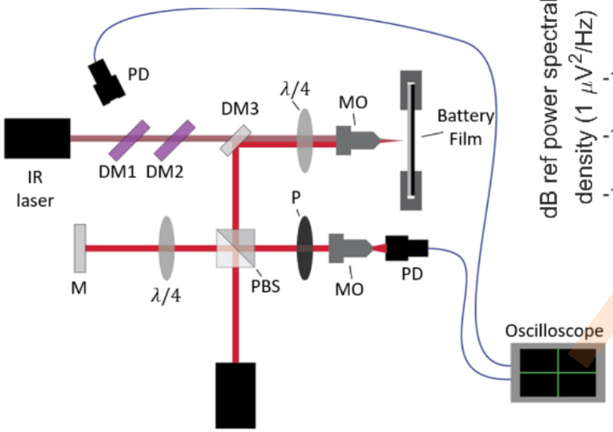
Localized ionic conductivity measurements of a commercial LCO electrode (above map) were obtained with a newly fabricated probe

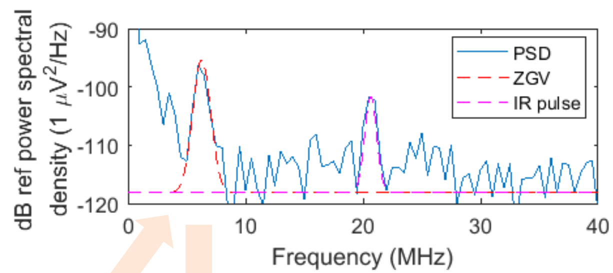




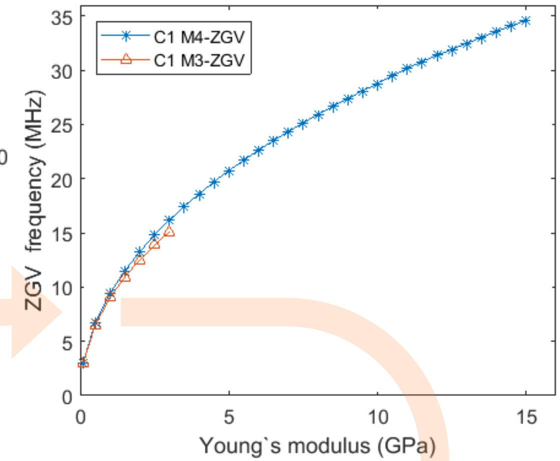
The new probe for localized ionic conductivity was inverted and attached to the production-ready stage to automate collection of localized ionic conductivity.

Technical Accomplishment: Localized Coating Mechanical Measurement by Interferometry

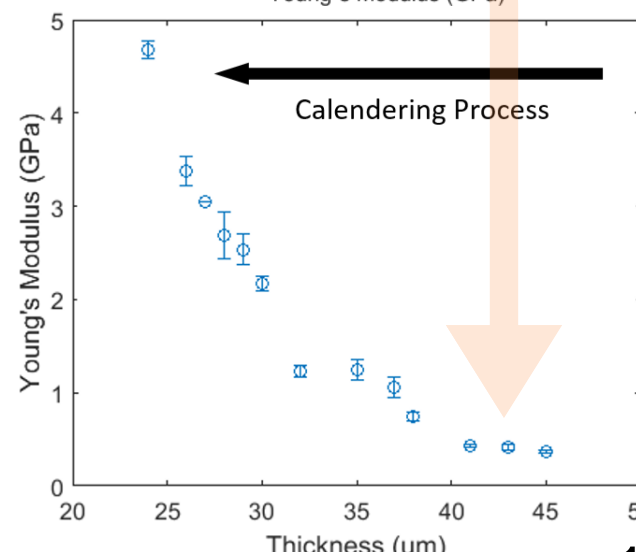




Calculated sensitivity to Young's Modulus

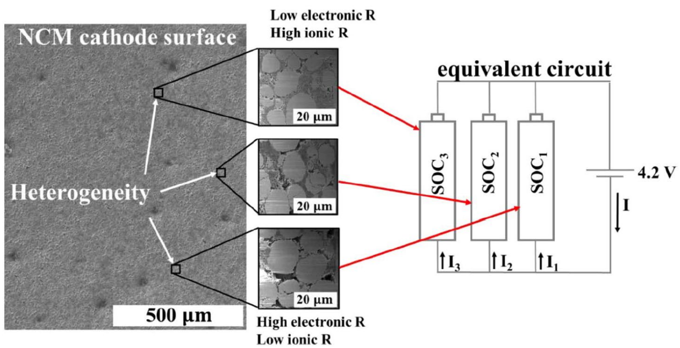


Infrared laser pulses were used to excite localized zero-group-velocity Lamb wave modes in the battery film and vibration responses were recorded by a laser interferometer. By analyzing the response, the Young's modulus of the battery coating was estimated. As a battery film was repeatedly calendered, the Young's modulus of the coating increased significantly. This demonstrates a technical path towards mapping localized mechanical properties of coatings.

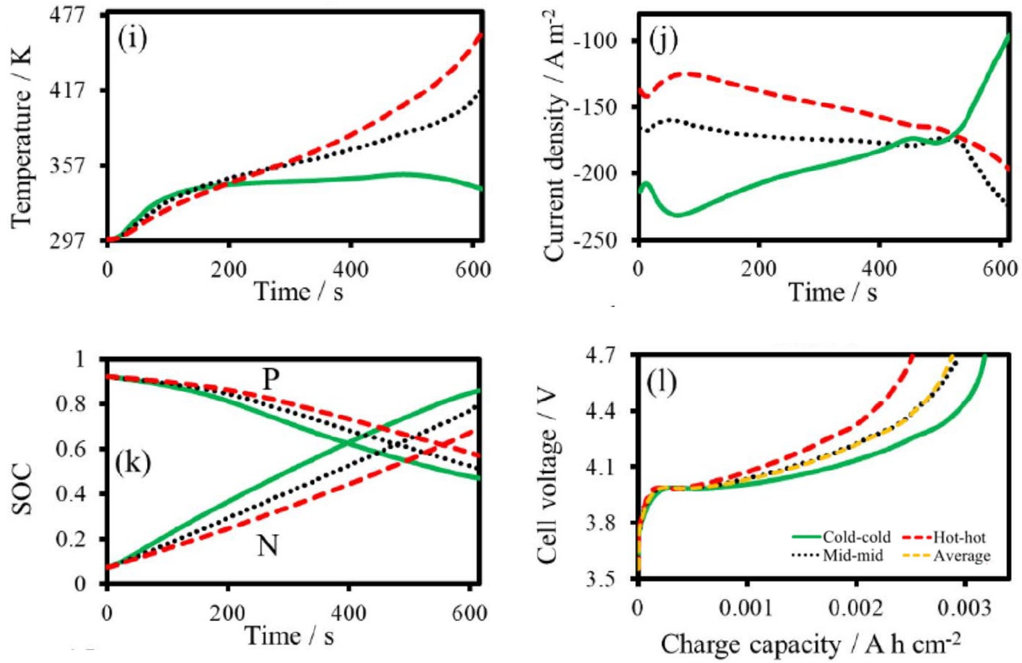


Technical Accomplishment: Predict Effect of Heterogeneity on Fast Charging

A Newman-type model was created to predict the effects of heterogeneity on cell-level performance



SEM/FIB images of three dissimilar regions (left) and a schematic of parallel heterogeneity model (right).[1]

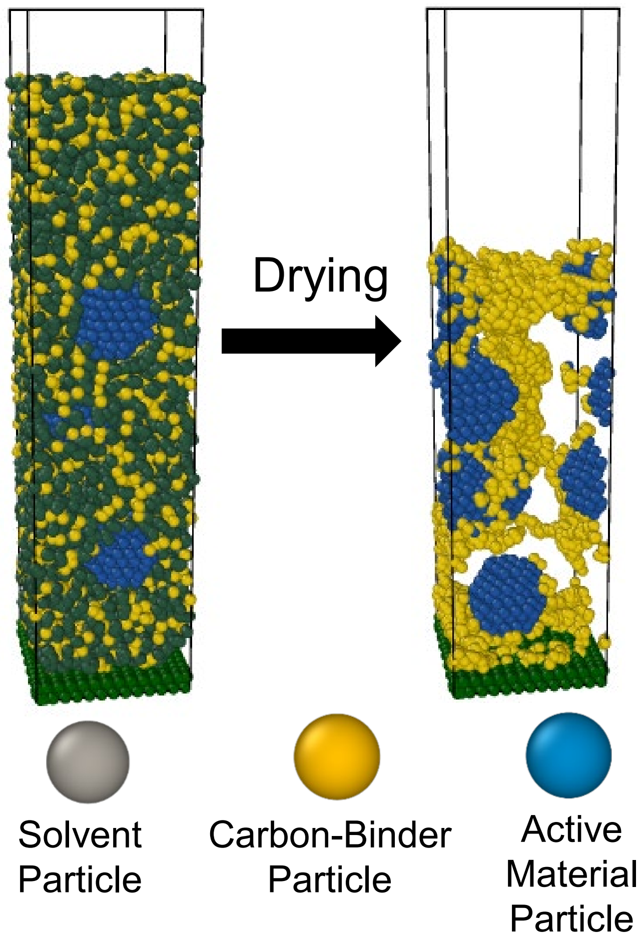


Cell performance curves for the fast-charging aligned-electrode-resistances case (hot-hot, middle-middle, and cold-cold). Hot, middle, cold means high, middle, low resistance respectively for each electrode. [1]

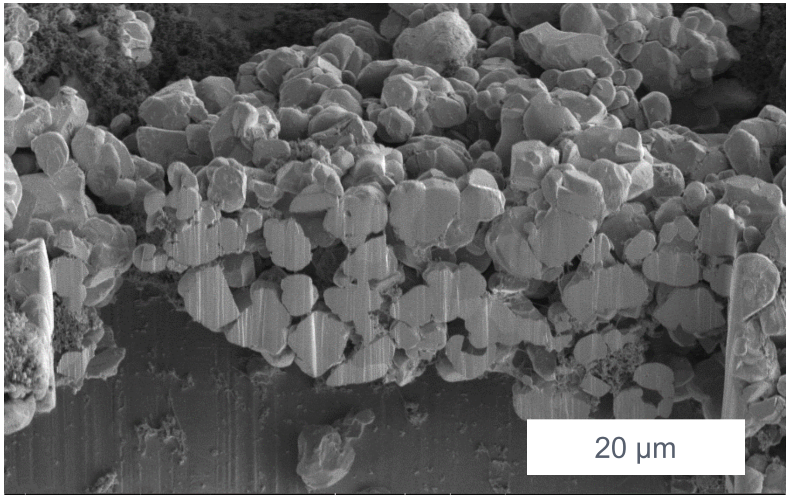
[1] Forouzan et al. "Modeling the effects of electrode microstructural heterogeneities on Li-ion battery performance and lifetime." *J. Electrochem. Soc.* 165 (2018): A2127-A2144.

Technical Accomplishment: Improved Microstructure Prediction of Drying Process

Drying process simulation using Smoothed Particle Hydrodynamics (SPH) in LAMMPS

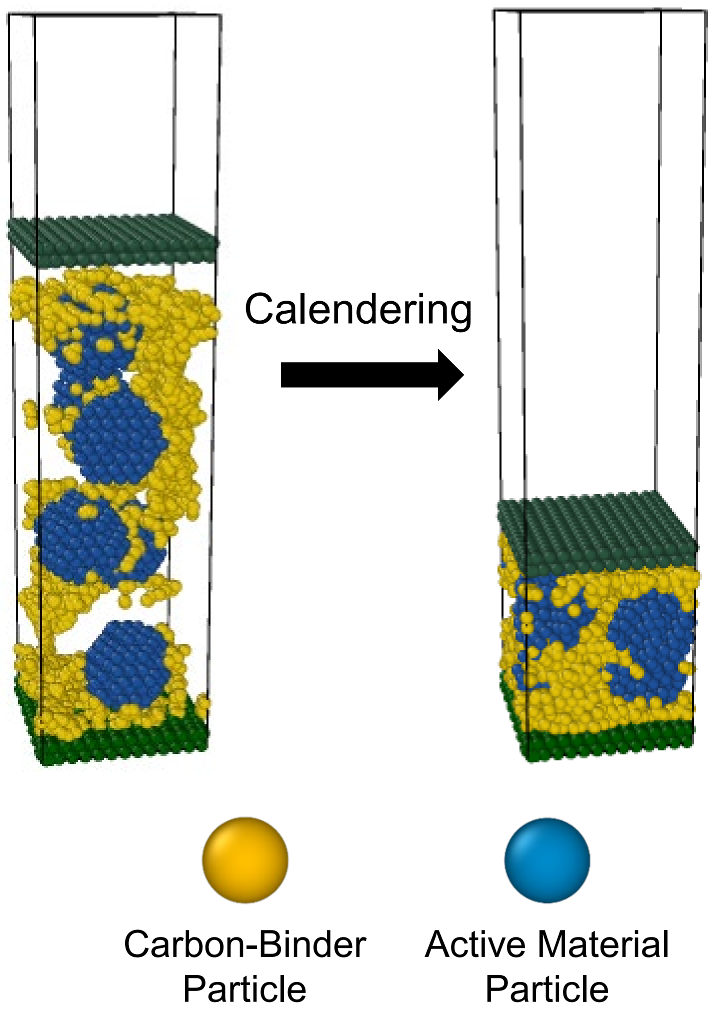


To validate the model, it was compared to images of the particle structure of the mixed slurry, obtained by a freeze drying technique, followed by SEM/FIB



SPH solves the Navier-Stokes equations on the particles, which are smoothed representations of solids or liquids

TECHNICAL ACCOMPLISHMENT: IMPROVED MICROSTRUCTURE PREDICTION OF CALENDERING



	Porosity after drying	Porosity after calendering
Experiment	55-65 %	30-35%
Simulation	61%	30%

The SPH model can be tuned to exactly represent experimental porosities after drying and after calendering.

The model will continue to be improved through FY19 (milestone 4Q19).

Responses to Previous Year Reviewers' Comments

BYU

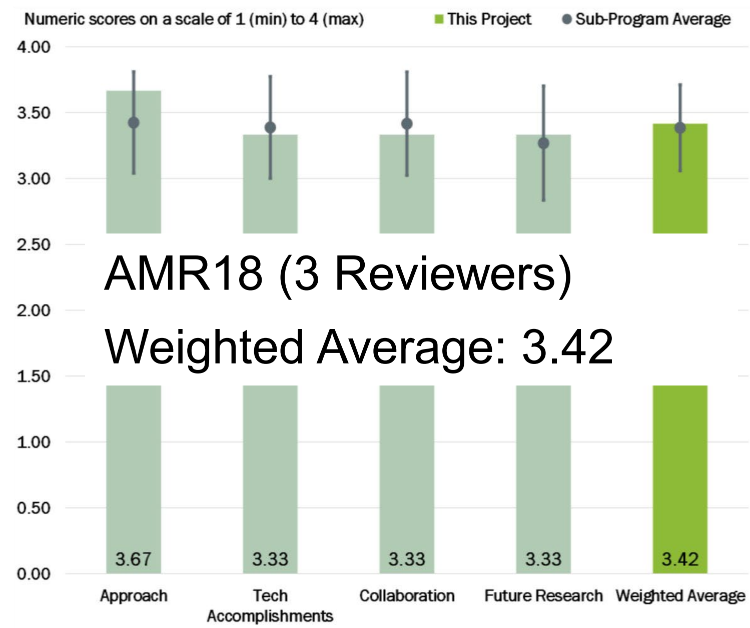
This project was favorably reviewed during AMR18, receiving mostly positive comments, including, "the project team continues to do an outstanding job of developing a new technique allowing a better understanding of the effects of electrode heterogeneity of cell performance." Responses to the main concerns are as follows:

1. Industrial collaborations:

   This year results were presented from materials provided by K2, Hydro-Québec, as well as Argonne National Laboratory. Other active industrial collaborators have also provided materials whose analyses have been shared privately.

2. Criticism of simulations:

   Because the drying conditions and drying technologies significantly affect the porous structure of the electrode film, a number of experiments (including a new technique for freeze-drying) were developed and performed this year to generate relevant data to improve the fidelity of the simulations.



Collaborations and Coordination

Non-contract partnerships and research collaborations involving exchange of battery materials and expertise

- Navitas Systems (Mike Wixom) – supplied materials for testing, submitted joint SBIR proposal
- Eagle Picher (Rob Gitzendanner) – supplied materials for testing
- NREL (Kandler Smith) – supplied materials for testing, joint publication with a large collaborative group
- K2 – supplied cells for cycle life testing
- Hydro-Québec (Chisu Kim) – supplied materials for cycle life testing
- [Undisclosed large EV manufacturer] – supplied materials for testing
- ANL (Daniel Abraham and Bryant Polzin) – supplied materials for testing
- Utah State University (Tianbiao Liu) – supplied materials for testing
- Missouri S&T (James Claypool) – purchased BYU conductivity probe
- UC Irvine (Iryna Zenyuk) – purchased BYU conductivity probe

Remaining Challenges and Barriers

- Continued development of localized ionic conductivity probe to determine heterogeneity for additional materials
- Continued development of new SPH microstructure model that is validated with experimental drying, microstructure, and conductivity data
- Adaptation of new acoustic probe to localized mapping of film stiffness
- Continued measurements on commercial-grade electrodes to quantify effects of different manufacturing processes (e.g. drying method, calendering), aging, and cycling

Proposed Future Research

2019

- **3Q**: Create design package for commercialization of the conductivity probe including associated control and computing hardware. *Justification:* This milestone will lead to a modular probe system prototype that can be replicated in order to enable scalable testing of electrode samples. This will enable researchers at BYU to attract additional interest and funding in order to commercialize the technology.
- **4Q**: Demonstrate ability of particle model to faithfully generate structures resulting from the drying processes. *Justification:* The fidelity of the model needs to be further improved to better match commercial drying steps. Achievement of this milestone will allow greater adoption of the simulation techniques to industry and academic development. Calendering simulations are also being conducted using the same model and will similarly be compared to experiment.
- Milestones for this project end September 2019 (work will continue until December 2019 due to an initial delay in the contract).

Any proposed future work is subject to change based on funding levels.

SUMMARY

Deliverables after first 88% of project time

- Flex probe for conductivity measurements has been fabricated and validated. This probe has been used to better understand electrode spatial heterogeneities and property changes with cycling.
- Significant progress has been made on other diagnostic tools (acoustic probe, ionic probe, and large-format positioning system), and refinement of microstructure prediction model.
- Multiple industrial partners have been sharing electrode samples with BYU in order to benefit from the unique information these tools provide. Significant progress has been made toward commercializing the probe technology.

How this will improve battery manufacturing and therefore reduce energy costs, increase energy security, and provide clean energy technology

- Commercial-grade electrodes have significant spatial differences in conductivity due to variability on the mm and smaller length scales. These variabilities require overdesign of electrodes to achieve satisfactory performance.
- The suite of tools can quantify these differences and enable real-time quality control in roll-to-roll processing. Improved manufacturing will drive down costs, improve electrode utilization, and improve cycle life. There is also the possibility of opening new routes to needed technologies such as fast charging.